Sulfonate Protecting Groups: Synthesis of D- and L-*myo*-Inositol-1,3,4,5-tetrakisphosphate Precursors by a Novel Silver(I) Oxide-Mediated *O*-Alkylation of 2,4(6)-Di-*O*-acyl-6(4)-*O*-sulfonyl-*myo*-Inositol 1,3,5-Orthoformate Derivatives Through Intramolecular Assistance of the Sulfonyl Group

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Keywords: Cyclitol / Inositol / Neighboring-group effects / Protecting groups / Signal transduction

Alkylation of racemic 2,4-di-*O*-acyl-6-*O*-sulfonyl-*myo*-inositol 1,3,5-orthoformates mediated by silver(I) oxide affords the corresponding racemic 2,4-di-*O*-alkyl-6-*O*-sulfonyl-*myo*-inositol 1,3,5-orthoformates in good yields. Control experiments suggest that these unusual reactions are due to intramolecular assistance by the sulfonyl group. *O*-Alkylation reactions of *myo*-inositol 1,3,5-orthoformate derivatives provide a new route for the synthesis of important ether derivatives of *myo*-inositol, which are intermediates for the preparation of phosphoinositols. The utility of this method is demonstrated by the preparation of D- and L-2,4-di-*O*-benzyl-*myo*-inositols, which were obtained by benzylation of 2,4-di-*O*-benzoyl-6-*O*-camphorsulfonyl-*myo*-inositol 1,3,5-orthoformate and 2,6-di-*O*-benzoyl-4-*O*-camphorsulfonyl-*myo*-inositol 1,3,5-orthoformate.

Introduction

The discovery of the cellular signal transduction mechanism mediated by *myo*-inositol phosphates is regarded as one of the most important in biology.[1] In particular, D-*myo*-inositol-1,4,5-trisphosphate [Ins(1,4,5)P_3] functions as a second messenger and D-*myo*-inositol-1,3,4,5-tetrakisphosphate [Ins(1,3,4,5)P_4], which is produced by the phosphorylation of Ins(1,4,5)P_3 in cells, has been shown to facilitate the activation of the store-operated calcium current and to provide both facilitatory and inhibitory feedback on calcium signaling.[2] Continued efforts in unraveling the biological roles of phosphoinositols and associated lipids, as well as their glycosylated derivatives, have revived the interest in the chemistry of inositols over the last decade.[3] Most syntheses of biologically relevant inositol derivatives starting from the naturally occurring *myo*-inositol have used ketals for the initial protection of hydroxyl groups, but increasingly their protection as orthoesters is being used[4] for the synthesis of phosphoinositols, cyclitol derivatives, and cyclitol-based metal complexing agents. In addition to their synthetic utility, orthoesters of *myo*-inositol are interesting as they exhibit unusual reactions because of their rigid adamantane-like structures. As part of an ongoing program on the chemistry of cyclitols, we have shown recently[5] that sulfonate groups can be utilized for the protection of *myo*-inositol hydroxyl groups. Herein, we present results to show that the camphorsulfonyl group can be utilized for the protection, as well as resolution, of *myo*-inositol orthoester derivatives.

Results and Discussion

During our efforts to develop simpler methods for the preparation of *O*-protected inositol derivatives, we found[4] that racemic 2,4-di-*O*-benzoyl-*myo*-inositol 1,3,5-orthoformate and its sulfonylated derivatives undergo alcoholysis in the presence of silver(I) oxide and silver halide to yield the corresponding 4,6- and 2,4-diols, respectively. We had observed earlier[6] that *O*-acyl-*myo*-inositol orthoformate derivatives could be alkylated with alkyl halides in the presence of silver(I) oxide to yield the corresponding 4,6-diethers. These results prompted us to subject the sulfonates **1**−**4** to alkylation with alkyl halides in the presence of silver(I) oxide.

The sulfonates **1**−**4** (Scheme 1) were prepared by sulfonylation of racemic 2,4-di-*O*-benzoyl-*myo*-inositol 1,3,5-or-

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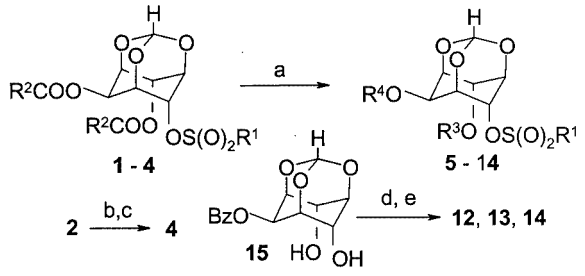
thoformate as reported earlier.[4] The racemic diacetate **4** was prepared by aminolysis of the racemic dibenzoate **2**, followed by acetylation with acetic anhydride in pyridine. Treatment of the sulfonates **1**−**4** with excess alkyl bromide or alkyl iodide in the presence of excess silver(I) oxide in DMF, followed by chromatography, afforded the corresponding dialkyl ethers **5**−**11** in moderate to good yields. Methylation of the sulfonates **1** and **3** with methyl iodide in the presence of silver(I) oxide resulted in methylation also on the carbon atom carrying the sulfur atom, in addition to *O*-alkylation at C-2 and C-4(6) positions. Since these *C*-methylated derivatives were not



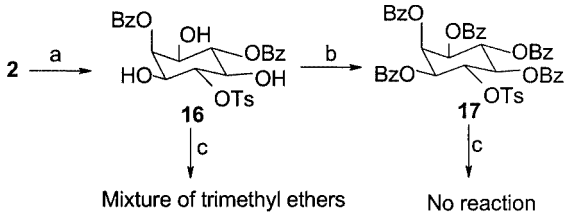
	R^1	R^2	R^3	R^4
1	Me	Ph		
2	*p*-tolyl	Ph		
3	(*1S*)-10-camphoryl	Ph		
4	*p*-tolyl	Me		
5	Me		Bn	Bn
6	Me		Allyl	Allyl
7	*p*-tolyl		Bn	Bn
8	*p*-tolyl		Allyl	Allyl
9	*p*-tolyl		Me	Me
10	(*1S*)-10-camphoryl		Bn	Bn
11	(*1S*)-10-camphoryl		Allyl	Allyl
12	Me		Bn	Bz
13	*p*-tolyl		Bn	Bz
14	(*1S*)-10-camphoryl		Bn	Bz

Scheme 1. Reagents and conditions; a) DMF, Ag_2O, alkyl halide; b) *tert*-butylamine, methanol, reflux; c) Ac_2O, pyridine; d) BnBr, K_2CO_3, DMF; e) R^1SO_2Cl, triethylamine. Compounds **3**, **10**, **11**, and **14** are mixture of diastereoisomers.

synthetically useful, they were not rigorously characterized. Alkyl chlorides, however, failed to alkylate the sulfonates **1**−**4**. Treatment of the sulfonates **1** and **2** with silver(I) oxide alone in DMF did not result in any reaction occurring and the starting materials were recovered quantitatively.

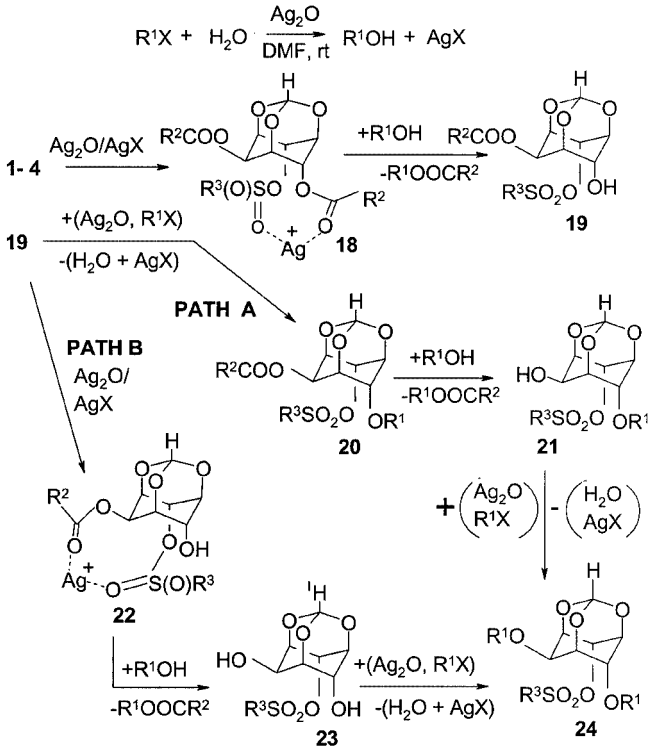
We established that the ester groups in sulfonates **1**−**4** undergo cleavage and alkylation sequentially — first the axial C-4(6) ester followed by the equatorial C-2 ester (however, see Scheme 3) — by carrying out their alkylations in the presence of lesser amounts of silver(I) oxide. For example, reaction of the mesylate **1** with benzyl bromide in the presence of smaller amount of silver(I) oxide gave a mixture of diether **5** and the monoether **12**. The structures of the monobenzyl ethers **12**−**14** were established by unambiguous syntheses starting from the known diol **15**. Mono *O*-benzylation of **15**[7] followed by sulfonylation with the required sulfonyl chloride gave the corresponding monoethers **12**−**14**.

A comparison of the alkylation of the sulfonates **1**−**4** with that of racemic 2,4-di-*O*-benzoyl-*myo*-inositol 1,3,5-orthoformate, which we reported earlier,[6] suggests that the cleavage and alkylation of the equatorial ester group at C-2 in **1**−**4** is due to the presence of the sulfonyl group, a feature that was observed during their methanolysis.[4] We showed that the relative orientation of the ester and the sulfonyl groups (as in **1**−**4**), as well as the presence of the rigid orthoformate moiety, are essential for the conversion of **1**−**4** to the corresponding diethers **5**−**11** by subjecting the triol **16** and the pentabenzoate **17** (Scheme 2) to methylation in the presence of silver(I) oxide. The triol **16** gave a mixture of trimethyl ethers (resulting from migration of the benzoyl groups, as revealed by ^{1}H NMR spectroscopy of the mixture of products) while the pentabenzoate **17** remained unaffected. Cleavage and *O*-alkylation of the benzoates in **16** and **17** was not observed. These results showed that the benzoates in **16** and **17** were stable to alkylation conditions in the presence of silver(I) oxide. All these results are in agreement with our earlier results[4] on the methanolysis of the sulfonates **1**−**4** in the presence of silver(I) oxide and silver halide. Intramolecular assistance by functional groups in small polyfunctional molecules, which leads to unexpected rates and/or product formation, is well documented in the literature.[8]



Scheme 2. Reagents and conditions: a) Methanol, *p*-TsOH; b) BzCl, pyridine; c) DMF, MeI, Ag_2O

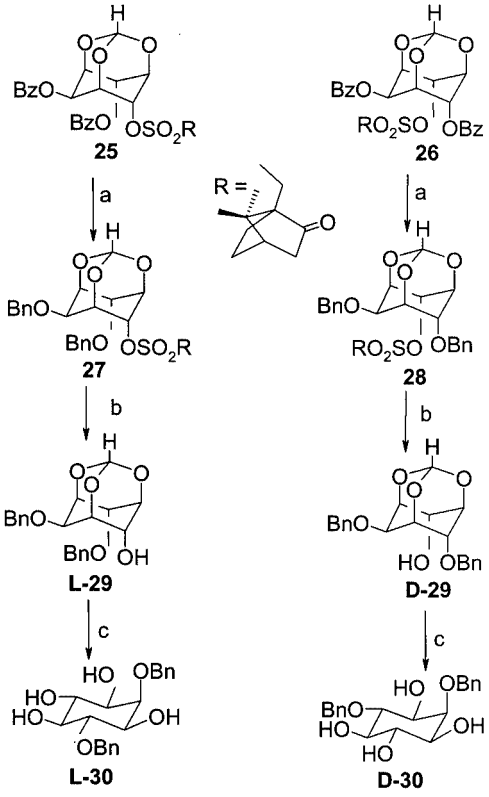
A possible explanation (Scheme 3) for this one-pot conversion of diesters **1**−**4** to the corresponding diethers **5**−**11** can be arrived at by considering the results of solvolysis of **1**−**3** in the presence of silver(I) oxide and silver halides that we reported[4] recently. Silver(I) oxide/silver halide-mediated alcoholysis of racemic diesters **1**−**3** yields the corresponding racemic diols **23**. The catalytic efficiency of the silver halides to bring about solvolysis of **1**−**3** decreased in the order AgI > AgBr > AgCl. In light of these results, it is appropriate to consider the conversion of the dibenzoates **1**−**4** to the corresponding diols **23** by alcoholysis, resulting from minor amounts of alcohol generated from the alkyl halides in the presence of silver(I) oxide,[9] and subsequent alkylation to form the diethers **24**. Hence, the conversion of dibenzoates **1**−**4** to the corresponding diethers **24** appears to be a multistep process: (i) generation of small amounts of alcohol and silver halide from silver(I) oxide and alkyl halide (silver(I) oxide is known to retain varying amounts of adsorbed water, depending on the method of its preparation, and that these adsorbed water molecules cannot be



Scheme 3

removed even by heating to high temperatures); (ii) intramolecular sulfonyl group-assisted alcoholysis of benzoates in **1**−**4** to form the alcohols **19**, **21**, and **23**;[4] (iii) *O*-alkylation of **19**, **21**, and **23** in the presence of silver(I) oxide to yield the diethers **24**. Once this reaction is initiated, water produced on the surface of silver(I) oxide by alkylation of free hydroxyl groups (in **19**, **21**, and **23**), could result in further hydrolysis of the alkyl halide (to the corresponding alcohol, step (i) above). This cycle repeats until all the esters are converted into the corresponding ethers. The possible sequence of reactions leading to the formation of diethers **24** is shown in Scheme 3. Failure of alkyl chlorides to alkylate the diesters **1**−**4** could be due to the lower catalytic efficiency of silver chloride[4] generated in situ, in bringing about the alcoholysis of the diesters **1**−**4**. Although it seems possible that hydrolysis of the esters in **1**−**4** to the corresponding alcohols **19**, **21**, or **23** (by water adsorbed on the surface of silver oxide) might occur prior to their alkylation, the contribution of this pathway to the overall reaction is not considerable. We have shown earlier[4] that relative facility of hydrolysis of the diesters **1**−**4** in the presence of silver(I) oxide and silver halide is much lower than their alcoholysis under comparable conditions. Even though monoethers **20** were isolated in some experiments, this observation does not establish their sole intermediacy during these alkylation reactions. The occurrence of parallel competing reaction pathways (Scheme 3, PATH A and PATH B) leading to the diethers **24** as the final product cannot be ruled out. The extent of operation of PATH A and PATH B could depend on the relative rates and facility of individual steps in Scheme 3.

To achieve the formal synthesis of both D- and L-Ins(1,3,4,5)P_4 (Scheme 4), diastereoisomeric camphorsulfonates **25** and **26** were separated by flash column chromatography. The crystal structure of **26** was solved to establish the diastereoisomers' absolute configurations. The diastereoisomers **25** and **26** were converted separately into the corresponding dibenzyl ethers **27** and **28** by reaction with benzyl bromide in the presence of silver(I) oxide. The camphorsulfonate group in **27** and **28** was removed by heating with sodium methoxide in methanol under reflux to yield the enantiomeric dibenzyl ethers **L-29** and **D-29**. It is possible to regenerate the *myo*-inositol orthoformate hydroxyl groups by solvolysis of its sulfonate units, since their rigid adamantane-like framework forces the solvolysis to proceed with retention of configuration.[10] Also, S−O bond cleavage during solvolysis of the sulfonates **27** and **28** cannot be ruled out. Finally, the orthoformate moiety in **L-29** and **D-29** was cleaved with aqueous trifluoroacetic acid to obtain the dibenzyl ethers **l-30** and **d-30**. A comparison of the overall yields reported in the literature[11] for the preparation of **L-30** and **D-30** from *myo*-inositol with those of the present method, shows that this current approach is simpler and higher yielding (28% for both D- and L-isomers) than most reports, and is similar to the method of Laumen and Ghisalba.[11e] As the resolution is carried out early in the synthetic scheme, it is possible to adopt these intermediates for the preparation of other useful derivatives of *myo*-inositol.



Scheme 4. Reagents and conditions: a) BnBr, Ag_2O, DMF, room temp., 80 h; b) NaOMe, methanol, reflux, 24 h; c) aq. TFA, 24 h

In conclusion, we have presented results on the sulfonyl group-assisted *O*-alkylation of *myo*-inositol orthoformate derivatives in the presence of silver(I) oxide, and the application of these new reactions in the synthesis of both the enantiomers of 2,4-di-*O*-benzyl-*myo*-inositol, which are precursors for the preparation of D- and L-Ins(1,3,4,5)P_4. In the work described here, the camphorsulfonyl group serves three purposes: (a) it is a protecting group for C-4(6) hydroxyl group of *myo*-inositol; (b) it provides intramolecular assistance for the cleavage of the esters to generate the corresponding alcohol; and (c) it is a resolving agent for racemic 2,4-di-*O*-benzoyl-*myo*-inositol 1,3,5-orthoformate.[6] Presently we are exploring the possibility of using the new findings reported here for the synthesis of other cyclitol derivatives, which will be reported in due course.

Experimental Section

General: For general experimental conditions see ref.[4,6b] (1*S*)-(+)-10-Camphorsulfonyl chloride,[12] silver(I) oxide,[6c] racemic 2-*O*-benzoyl-4-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate,[7] sulfonates[4] **1**−**4** and the pentabenzoate[4] **17** were prepared by literature procedures. All of the compounds (except those shown in Scheme 4) are racemic or mixtures of diastereoisomers, but only one of the enantiomers (or diastereoisomers) is shown in the first three schemes for brevity and convenience.

Racemic 2,4-Di-*O*-acetyl-6-*O*-tosyl-*myo*-inositol 1,3,5-orthoformate (4): The dibenzoate **2** (0.180 g, 0.34 mmol) was heated with *tert*-butylamine in methanol under reflux for 5 h. The residue obtained after removal of volatile liquids was dissolved in pyridine (1 mL), a solution of acetic anhydride (0.430 g, 4.21 mmol) in pyridine (1 mL) was added dropwise at 0 °C, and then the mixture stirred for 24 h. The reaction mixture was poured into an ice-cold solution of sodium bicarbonate and the solid that precipitated was filtered and washed with water. The precipitate was dissolved in ethyl acetate and washed successively with dilute HCl, water, and brine. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography to obtain **4** (0.140 g, 96%), m.p. 114−116 °C. IR (nujol): $\tilde{\nu}$ = 1700, 1720 (C=O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.10 (s, 3 H, MeCO), 2.25 (s, 3 H, MeCO), 2.50 (s, 3 H, ArMe), 4.15−4.25 (m, 1 H), 4.30−4.40 (m, 1 H), 4.55−4.65 (m, 1 H), 5.00−5.15 (m, 1 H, 4-H), 5.20−5.30 (d, *J* = 6.0 Hz, 1 H, 2-H), 5.40−5.50 (m, 1 H, 6-H), 5.55 (d, *J* = 1.5 Hz, 1 H, O_3CH), 7.40 (d, *J* = 8.0 Hz, 2 H, ArH), 7.85 (d, *J* = 8.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.3 (MeCO), 20.6 (MeCO), 21.4 (ArMe), 62.3, 66.2, 66.7, 68.6, 68.8, 71.8 (C1−C6), 102.5 (O_3C), 127.6, 129.9, 132.0, 145.5, 169.2 (C=O), 169.8 (C=O) ppm. $C_{18}H_{20}O_{10}S$ (428.4): calcd. C 50.47, H 4.67; found C 50.43, H 4.40%.

Alkylation of *myo*-Inositol Orthoformate Derivatives. General Procedure: *Myo*-inositol 1,3,5-orthoformate derivative **1**−**4** and the alkyl halide were dissolved in dry DMF and freshly prepared silver(I) oxide was added in portions over 10 minutes with vigorous stirring and external cooling with ice. Stirring was continued at room temperature until the starting material disappeared (maximum 80 h). The reaction mixture was filtered through a small column of Celite and the residue was washed with chloroform. The filtrate and washings were combined and washed with sodium cyanide solution (1%, 100 mL) and the aqueous layer was extracted with chloroform. The combined chloroform extract was washed successively with water and brine, dried over anhydrous sodium sulfate, and then the solvent was evaporated under reduced pressure. The products were isolated by column chromatography over silica gel.

Alkylation of Racemic 2,4-Di-*O*-benzoyl-6-*O*-mesyl-*myo*-inositol 1,3,5-Orthoformate (1). (a) With Benzyl Bromide, Procedure A: The mesylate **1** (0.232 g, 0.49 mmol) was reacted with benzyl bromide (1.2 mL, 10.09 mmol) and silver(I) oxide (1.160 g, 5.00 mmol) in DMF (3 mL) to obtain the dibenzyl ether **5** (0.200 g, 92%) as a gum. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.85 (s, 3 H, Me), 3.95 (m, 1 H), 4.30−4.40 (m, 2 H), 4.40−4.50 (m, 1 H), 4.50−4.70 (m, 3 H, OCH_2 and Ins H), 4.70−4.80 (q, *J* = 12.0 Hz, 2 H, OCH_2), 5.40 (t, *J* = 4.0 Hz, 1 H, H-4), 5.60 (s, 1 H, O_3CH), 7.10−7.60 (m, 10 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 37.9 (Me), 65.9, 67.2, 69.4, 69.8 (Ins Cs), 71.3 (CH_2), 71.8 (CH_2), 72.8 (Ins C), 102.7 (O_3C), 127.3, 127.8, 128.2, 137.0, 137.2 ppm. $C_{22}H_{24}O_8S$ (448.5): calcd. C 58.69, H 5.37; found C 58.93, H 5.53%.

(b) With Benzyl Bromide, Procedure B: The mesylate **1** (0.464 g, 0.97 mmol) was reacted with benzyl bromide (1.2 mL, 10.09 mmol) and silver(I) oxide (1.160 g, 5.00 mmol) in DMF (6 mL). The dibenzyl ether **5** (0.150 g, 34%) and the monobenzyl ether **12** (0.045 g, 10%) were obtained along with the starting material **1** (0.23 g, 49%). Data for **12**: m.p. 166−168 °C. IR: $\tilde{\nu}$ = 1700 (C=O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.90 (s, 3 H, Me), 4.45 (m, 1 H), 4.55 (m, 2 H), 4.7 (m, 3 H, OCH_2 and Ins H), 5.40−5.55 (m, 2 H, H-2, H-4), 5.60 (s, 1 H, HCO_3), 7.30−7.45 (m, 5 H, Ph), 7.45−7.55 (m, 2 H, PhCO *m*-H), 7.55−7.65 (m, 1 H, PhCO, *p*-H), 8.15 (d, *J* = 8.0 Hz, 2 H, PhCO *o*-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 39.0 (Me), 64.0, 68.0, 70.0, 70.5 (Ins Cs), 72.0 (CH_2), 73.0 (Ins C), 103.0 (CO_3), 128.0, 128.5, 129.0, 130.0, 130.5, 134.0, 137.0, 167.0 (CO) ppm. $C_{22}H_{22}O_9S$ (462.5): calcd. C 57.14, H 4.79; found C 56.82, H 4.83%.

(c) With Allyl Bromide: The mesylate **1** (0.460 g, 0.97 mmol) was alkylated with allyl bromide (1 mL, 11.55 mmol) and silver(I) oxide (1.160 g, 5.00 mmol) in DMF (4 mL) to yield the diallyl ether **6** as a gum (0.280 g, 83%). ^1H NMR (200 MHz, $CDCl_3$): δ = 3.10 (s, 3 H, Me), 3.90 (d, *J* = 1.4 Hz, 1 H), 4.00−4.15 (m, 2 H), 4.15−4.25 (dd, *J* = 5.9 Hz, 1.5 Hz, 2 H), 4.30−4.40 (m, 2 H), 4.40−4.50 (q, *J* = 2.0 Hz, 1 H), 4.55−4.60 (m, 1 H), 5.20−5.40 (m, 5 H, $=CH_2$ and H-4), 5.55 (d, *J* = 1.1 Hz, 1 H, O_3CH), 5.75−6.10 (m, 2 H, =CH) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 38.2 (Me), 66.3, 67.3, 69.5, 69.9 (Ins Cs), 70.4 (CH_2), 72.0, 72.7 (Ins Cs), 102.7 (CO_3), 117.5 ($=CH_2$), 117.8 ($=CH_2$), 133.6 (=CH), 134.0 (=CH) ppm. $C_{14}H_{20}O_8S$ (348.4): calcd. C 48.27, H 5.79; found C 48.55, H 5.95%.

Alkylation of Racemic 2,4-Di-*O*-benzoyl-6-*O*-tosyl-*myo*-inositol 1,3,5-Orthoformate (2). (a) With Benzyl Bromide: The tosylate **2** (0.350 g, 0.63 mmol) was reacted with benzyl bromide (0.76 mL, 6.30 mmol) and silver(I) oxide (0.735 g, 3.17 mmol) in DMF (4 mL). The mono benzyl ether **13** (0.100 g, 29%) was obtained as a crystalline solid while the dibenzyl ether **7** (0.22 g, 66%) was obtained as a colorless gum. Data for **7**: ^1H NMR (200 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, Me), 3.95 (d, *J* = 2.2 Hz, 1 H), 4.15−4.35 (m, 3 H), 4.35−4.40 (m, 1 H), 4.45−4.65 (AB q, *J* = 10.1 Hz, 2 H, CH_2), 4.60 (s, 2 H, CH_2), 5.15 (dt, *J* = 6.3, 1.2 Hz, 1 H), 5.55 (d, *J* = 1.2 Hz, 1 H, HCO_3), 7.10−7.50 (m, 12 H, ArH), 7.75 (d, *J* = 9.0 Hz, 2 H, Ts-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.5 (Me), 66.4, 66.8, 67.3, 69.5, 70.0 (Ins Cs), 71.2 (CH_2), 71.5 (CH_2), 72.8 (Ins C), 102.8 (CO_3), 127.4, 127.7, 127.8, 127.9, 128.3, 129.7, 129.9, 132.6, 137.0, 137.3, 145.3 ppm. $C_{28}H_{28}O_8S$ (526.6): calcd. C 64.11, H 5.38; found C 63.71, H 5.76%. Data for **13**: m.p. 108−109

°C. IR: $\tilde{\nu}$ = 1700 (C=O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, Me), 4.30−4.40 (m, 2 H), 4.40−4.55 (m, 2 H), 4.60−4.80 (q, *J* = 15.9 Hz, 2 H, CH_2), 5.30 (t, *J* = 5.1 Hz, 1 H, H-4), 5.45 (m, 1 H, H-2), 5.55 (s, 1 H, HCO_3), 7.20−7.70 (m, 10 H, Ph), 7.80 (d, *J* = 8.9 Hz, 2 H, Ts-H), 8.15 (d, *J* = 8.1 Hz, 2 H, PhCO *o*-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.5 (Me), 63.4, 67.8, 69.7, 69.9 (Ins Cs), 71.5 (CH_2), 72.4, 72.7 (Ins Cs), 103.0 (CO_3), 127.7, 127.9, 128.4, 129.9, 133.2, 137.0, 145.2, 165.7 (C=O) ppm. $C_{28}H_{26}O_9S$ (538.6): calcd. C 62.43, H 4.87; found C 62.46, H 5.13%.

(b) With Allyl Bromide: The tosylate **2** (0.250 g, 0.45 mmol) was reacted with allyl bromide (0.50 mL, 5.72 mmol) and silver(I) oxide (0.520 g, 2.25 mmol) in DMF (2 mL) to obtain the diallyl ether **8** as a crystalline solid (0.180 g, 94%); m.p. 82−84 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, Me), 3.80 (m, 1 H), 3.90−4.40 (m, 8 H, OCH_2 and Ins H), 5.00−5.10 (m, 1 H), 5.15−5.30 (m, 3 H), 5.30−5.40 (m, 1 H), 5.45 (d, *J* = 1.6 Hz, 1 H, HCO_3), 5.70−6.05 (m, 2 H, =CH), 7.30−7.45 (d, *J* = 8.2 Hz, 2 H, Ts-H), 7.75 7.90 (d, *J* = 8.0 Hz, 2 H, Ts-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.6 (Me), 66.6, 67.4, 69.6 (Ins-Cs), 70.2 (OCH_2), 70.5 (OCH_2), 72.7, 73.1, 76.6 (Ins-Cs), 102.9 (O_3C), 117.6 (=CH_2), 117.8 (=CH_2), 127.9, 130.1, 132.9 (=CH), 133.8, 134.2, 145.5 ppm. $C_{20}H_{24}O_8S.H_2O$ (442.5): calcd. C 54.08, H 5.90; found C 53.96, H 5.81%.

(c) With Methyl Iodide: The tosylate **2** (0.280 g, 0.51 mmol) was methylated with silver(I) oxide (0.590 g, 2.55 mmol) and methyl iodide (0.31 mL, 4.98 mmol) in DMF (2 mL) to obtain the dimethyl ether **9** as a crystalline solid (0.150 g, 80%); m.p. 144−145 °C. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.50 (s, 3 H, Me), 3.40 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.65 (q, *J* = 7.2 Hz, 2.3 Hz, 1 H), 4.10−4.20 (m, 2 H), 4.35 (m, 1 H), 4.45 (m, 1 H), 5.10 (m, 1 H, H-6) 5.45 (d, *J* = 1.2 Hz, 1 H, HCO_3), 7.40 (d, *J* = 8.9 Hz, 2 H, Ts-H), 7.85 (d, *J* = 9.2 Hz, 2 H, Ts-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 21.5 (Me), 56.7 (OMe), 57.0 (OMe), 66.8, 68.4, 68.9, 69.0, 72.9, 74.7 (Ins Cs), 102.8 (CO_3), 127.8, 130.0, 132.7, 145.4 ppm. $C_{16}H_{20}O_8S$ (327.4): calcd. C 51.61, H 5.41; found C 51.39, H 5.60%.

Alkylation of 2,4(6)-Di-*O*-benzoyl-6(4)-*O*-[(1*S*)-10-camphorsulfonyl]-*myo*-inositol 1,3,5-Orthoformate (3, Mixture of Diastereoisomers). (a) With Benzyl Bromide: The camphorsulfonate **3** (0.250 g, 0.41 mmol) was reacted with benzyl bromide (1 mL, 8.41 mmol) and silver(I) oxide (0.950 g, 4.10 mmol) in DMF (2 mL) to obtain the monobenzyl ether **14** (0.025 g, 10%) and the dibenzyl ether 10 (0.144 g, 60%) both as mixture of diastereoisomers. Data for **10**: ^1H NMR (200 MHz, $CDCl_3$): δ = 0.75 (2 s, 3 H, Me), 1.05 (2 s, 3 H, Me), 1.15−1.45 (m, 1 H), 1.45−1.75 (m, 1 H), 1.80−2.15 (m, 3 H), 2.25−2.45 (m, 2 H), 2.85−3.00 (d, 1 H), 3.45−3.65 (dd, 1 H, SO_2CH_2), 4.00 (dd, 1 H, SO_2CH_2), 4.20−4.40 (m, 2 H), 4.40−4.85 (m, 6 H), 5.40−5.55 (m, 1 H), 5.55 (s, 1 H, HCO_3), 7.10−7.60 (m, 10 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.8 (Me), 25.0 (CH_2), 27.0 (CH_2), 42.6 (CH_2), 42.9, 48.1 (CH_2), 48.3 (CH_2), 48.5, 58.0, 66.3, 67.9, 70.0, 70.1, 70.4, 71.7, 72.6 (CH_2), 72.7 (CH_2), 73.4, 103.2 (CO_3), 127.5, 127.7, 128.1, 128.2, 128.4, 128.7, 137.5, 214.0 (C=O) ppm. $C_{31}H_{36}O_9S$ (584.7): calcd. C 63.66, H 6.21; found C 63.52, H 6.10%. Data for **14**: M.p. 62−64 °C. IR: $\tilde{\nu}$ = 1710, 1730 (C=O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.75−0.90 (2 s, 3 H, Me), 1.00−1.10 (2 s, 3 H, Me), 1.15−2.50 (m, 7 H), 3.00−3.15 (d, 1 H), 3.60−3.75 (2 d, 1 H), 4.40−4.85 (m, 6 H), 5.45−5.55 (m, 2 H), 5.60 (d, 1 H), 7.25−7.70 (m, 8 H), 8.15 (d, 2 H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.4 (Me), 24.6 (Me), 25.0 (Me), 26.8 (CH_2), 42.3 (CH_2), 42.6 (CH_2), 42.7 (CH_2), 48.0 (CH_2), 48.3 (CH_2), 48.5, 57.8, 63.4, 67.8, 69.5, 69.8, 71.6 (CH_2), 71.9, 72.7, 102.9 (CO_3), 127.7, 128.0, 128.4, 128.5, 129.4, 129.9, 133.4, 137.0, 165.8 (PhC=O), 213.9 (camphor C=O) ppm. $C_{31}H_{34}O_{10}S·0.5H_2O$ (607.7): calcd. C 61.26, H 5.81; found C 61.17, H 5.57%.

(b) With Allyl Bromide: The camphorsulfonate **3** (0.480 g, 0.78 mmol) was reacted with allyl bromide (1.4 mL, 16.18 mmol) and silver(I) oxide (1.800 g, 7.77 mmol) in DMF (4 mL) to obtain the diallyl ethers **11** (mixture of diastereoisomers) as a gum (0.270 g, 71%). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.85 (s, 3 H, Me), 1.10 (2 s, 3 H, Me), 1.35−1.50 (m, 1 H), 1.55−1.75 (m, 1 H), 1.95−2.20 (m, 3 H), 2.25−2.55 (m, 2 H), 2.95−3.10 (2 s, 1 H), 3.55−3.75 (dd, 1 H, H_2CSO_2), 3.80−3.95 (dd, 1 H, H_2CSO_2), 3.95−4.25 (m, 4 H), 4.25−4.40 (m, 2 H), 4.40−4.50 (m, 1 H), 4.55−4.65 (m, 1 H), 5.15−5.45 (m, 5 H, =CH_2 and H-4), 5.55 (d, 1 H, HCO_3), 5.75−6.15 (m, 2 H, =CH) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.2 (Me), 24.4 (CH_2), 26.4 (CH_2), 42.0 (CH_2), 42.3 (CH), 47.8 (CH_2), 57.5, 66.1, 67.2, 69.4, 69.8, 70.2, 72.1 (CH_2), 72.5, 102.5 (CO_3), 117.3 (=CH_2), 117.4 (=CH_2), 117.6, 133.5 (=CH), 133.9 (=CH), 213.5 (C=O) ppm. $C_{23}H_{32}O_9S$ (484.6): calcd. C 57.01, H 6.66; found C 57.33, H 6.87%.

Alkylation of Racemic 2,4-Di-*O*-acetyl-6-*O*-tosyl-*myo*-inositol 1,3,5-Orthoformate (4): The diacetate **4** (0.130 g, 0.30 mmol) was reacted with allyl bromide (0.3 mL, 3.47 mmol) and silver(I) oxide (0.350 g, 1.51 mmol) in DMF (2 mL) to obtain the diallyl ether **8** (0.070 g, 55%).

Synthesis of Racemic 2-*O*-benzoyl-4(6)-*O*-benzyl-6(4)-*O*-sulfonyl-*myo*-inositol 1,3,5-Orthoformates (12−14). General Procedure: Racemic 2-*O*-benzoyl-4-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate[7] was dissolved in pyridine (10 mL) and cooled to 0 °C. The sulfonyl chloride was added with stirring at 0 °C and then stirring was continued for 24 h at ambient temperature. The reaction mixture was diluted with chloroform or ethyl acetate, then washed with water, cold dilute HCl, saturated $NaHCO_3$ solution, and finally with brine. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The product was isolated either by crystallisation or by column chromatography.

Racemic 2-*O*-benzoyl-4-*O*-benzyl-6-*O*-mesyl-*myo*-inositol 1,3,5-Orthoformate (12): Racemic 2-*O*-benzoyl-4-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate (0.190 g, 0.49 mmol) was mesylated with mesyl chloride (0.2 mL, 2.58 mmol) in pyridine at 0 °C and the reaction mixture was stored in a refrigerator overnight. The mesylate **12** was isolated by crystallization from dichloromethane (0.210 g, 98%) after usual workup of the reaction mixture.

Racemic 2-*O*-benzoyl-4(6)-*O*-benzyl-6(4)-*O*-tosyl-*myo*-inositol 1,3,5-Orthoformate (13): Racemic 2-*O*-benzoyl-4-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate (0.288 g, 0.75 mmol) was tosylated with tosyl chloride (0.427 g, 2.24 mmol) in pyridine according to the general procedure. The tosylate **13** was isolated by column chromatography (0.400 g, 99%).

2-*O*-Benzoyl-4(6)-*O*-benzyl-6(4)-*O*-[*1(S)*-10-camphorsulfonyl]-*myo*-inositol 1,3,5-Orthoformate (14, Mixture of Diastereoisomers): Racemic 2-*O*-benzoyl-4-*O*-benzyl-*myo*-inositol 1,3,5-orthoformate (0.190 g, 0.49 mmol) was sulfonylated with camphorsulfonyl chloride (0.375 g, 1.50 mmol) in pyridine according to the general procedure. The camphorsulfonate **14** was isolated by column chromatography (0.290 g, 97%).

Racemic 2,4-Di-*O*-benzoyl-6-*O*-*p*-toluenesulfonyl-*myo*-inositol (16): The tosylate **2** (1.656 g, 3.00 mmol) was treated with *p*-toluenesul-

fonic acid monohydrate (1.710 g, 9.00 mmol) in methanol (15 mL) for 5 h at 60 °C. Methanol was evaporated and the residue obtained was chromatographed over silica gel to get **16** (1.500 g, 92%); m.p. 199−201 °C. IR: $\tilde{\nu}$ = 1680−1710 (C=O), 3300−3550 (OH) cm^{-1}. ^1H NMR (200 MHz, [D_6]DMSO): δ = 2.35 (s, 3 H, Me), 3.70 (t, *J* = 9.3 Hz, 1 H,), 3.90−4.00 (m, 2 H), 4.85 (t, *J* = 8.0 Hz, 1 H, H-4), 5.35 (t, *J* = 9.4 Hz, 1 H, H-6), 5.40 (d, *J* = 5.1 Hz, 1 H, OH), 5.45−5.60 (m, 3 H, 2 OH and H-2), 7.35 (d, *J* = 7.3 Hz, 2 H), 7.50 (t, *J* = 8.1 Hz, 2 H), 7.65 (t, *J* = 5.9 Hz, 3 H), 7.70 (d, *J* = 6.1 Hz, 1 H), 7.75 (d, *J* = 9.2 Hz, 2 H), 7.95 (d, *J* = 8.8 Hz, 2 H), 8.05 (d, *J* = 9.1 Hz, 2 H) ppm. ^{13}C NMR (50.3 MHz, [D_6]DMSO): δ = 21.0 (Me), 67.4, 70.0, 75.8, 76.0, 85.4 (Ins Cs), 127.7, 128.7, 129.3, 129.4, 130.6, 133.0, 133.2, 135.5, 143.7, 165.3 (C=O), 165.4 (C=O) ppm. $C_{27}H_{26}O_{10}S$ (542.6): calcd. C 59.77, H 4.83; found C 59.34, H 5.02%.

D-2,6-Di-*O*-benzoyl-4-*O*-[*1(S)*-10-camphorsulfonyl]-*myo*-inositol 1,3,5-Orthoformate (25) and D-2,4-Di-*O*-benzoyl-6-*O*-[(1*S*)-10-camphorsulfonyl]-*myo*-inositol 1,3,5-Orthoformate (26): The diastereoisomeric camphorsulfonates (mixture of diastereoisomers **3** prepared as in ref.[4]) were separated by flash column chromatography using ethyl acetate/light petroleum as eluent (1:9 v/v) to obtain diastereoisomers **25** and **26**. Data for **25**: m.p. 68−70 °C. $[\alpha]_D^{25}$ = −4.2 (*c* = 2.3, $CHCl_3$). IR: $\tilde{\nu}$ = 1728 (C=O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, Me), 1.01 (s, 3 H, Me), 1.35−1.50 (m, 1 H), 1.55−1.75 (m, 1 H), 1.80−2.10 (m, 3 H), 2.20−2.45 (m, 2 H), 2.90−3.00 (d, *J* = 14.2 Hz, 1 H, SO_2CH_2), 3.45−3.65 (d, *J* = 14.0 Hz, 1 H, SO_2CH_2), 4.55−4.80 (m, 2 H), 4.90 (m, 1 H), 5.50−5.65 (m, 2 H, H-2, H-4), 5.70 (d, *J* = 1.2 Hz, 1 H, HCO_3), 5.80−5.95 (m, 1 H, H-6), 7.35−7.70 (m, 6 H), 8.05−8.25 (m, 4 H, Ph *o*-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.2 (Me), 24.7 (CH_2), 26.6 (CH_2), 26.9 (CH_2), 42.1 (CH_2), 42.6, 47.8 (CH_2), 48.3 (CH_2), 57.8, 63.1, 67.5, 69.1, 69.4, 72.3, 102.9 (CO_3), 128.3, 128.4, 128.8, 129.3, 129.8, 133.3, 133.4, 164.9 (PhC=O), 165.7 (PhC=O), 213.4 (camphor C=O) ppm. $C_{31}H_{32}O_{11}S$ (612.6): calcd. C 60.76, H 5.23; found C 60.45, H 4.88%. Data for **26**: m.p. 165−168 °C. $[\alpha]_D^{25}$ = +35.0 (*c* = 2.5, $CHCl_3$). IR: $\tilde{\nu}$ = 1720−1740 (C=O) cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 0.75 (s, 3 H, Me), 0.96 (s, 3 H, Me), 1.40 −1.75 (m, 2 H), 1.80−2.10 (m, 3 H), 2.20−2.45 (m, 2 H), 2.89 (d, *J* = 15.1 Hz, 1 H, SO_2CH_2), 3.56 (d, *J* = 15.3 Hz, 1 H, SO_2CH_2), 4.60−4.70 (dd, *J* = 4.3 Hz, 1.9 Hz, 1 H), 4.70−4.80 (dd, *J* = 4.3 Hz, 2.1 Hz, 1 H), 4.80−4.95 (m, 1 H), 5.50−5.65 (m, 2 H, H-2, H-4), 5.70 (d, *J* = 1.0 Hz, 1 H, HCO_3), 5.80−5.95 (m, 1 H, H-4 or H-6), 7.35−7.70 (m, 6 H), 8.05−8.25 (m, 4 H, Ph *o*-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.4 (Me), 24.6 (CH_2), 26.6 (CH_2), 29.5 (CH_2), 42.2, 42.5 (CH_2), 48.0 (CH_2), 57.7, 63.1, 67.2, 67.4, 69.1, 69.7, 72.1, 102.9 (CO_3), 128.4, 128.5, 129.2, 130.0, 133.4, 133.6, 164.8 (PhC=O), 165.8 (PhC=O), 213.7 (camphor C=O) ppm. $C_{31}H_{32}O_{11}S$ (612.6): calcd. C 60.76, H 5.23; found C 60.41, H 5.62%.

L-2,4-Di-O-benzyl-*myo*-inositol (L-30): The camphorsulfonate **25** (0.200 g, 0.33 mmol) was reacted with benzyl bromide (0.4 mL, 3.36 mmol) and silver(I) oxide (0.760 g, 3.28 mmol) in DMF (1 mL) as in the case of **10**. The product was chromatographed over silica gel (eluent: 5% ethyl acetate/light petroleum) to yield the dibenzyl ether 27 (0.155 g, 81%).$[\alpha]_D^{25}$ = +11.2 (*c*= 2.05, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.75 (s, 3 H, Me), 1.00 (s, 3 H, Me), 1.25−1.45 (m, 1 H), 1.45−1.65 (m, 1 H), 1.80−2.05, (m, 2 H), 2.10 (t, *J* = 4.4 Hz, 1 H), 2.25−2.45 (m, 2 H), 2.90 (d, *J* = 14.8 Hz, 1 H, SO_2CH_2), 3.55 (d, *J* = 15.0 Hz, 1 H, SO_2CH_2), 3.95 (dd, *J* = 3.1 Hz, 1.1 Hz, 1 H), 4.25−4.32 (m, 1 H), 4.35−4.40 (m, 1 H), 4.40−4.55 (m, 2 H), 4.55−4.70 (m, 2 H, $PhCH_2$), 4.70−4.85 (AB q, *J* = 14.2 Hz, 4.3 Hz, 2 H, $PhCH_2$), 5.40−5.50 (m, 1 H, H-6), 5.55 (d, *J* = 1.5 Hz, 1 H, HCO_3), 7.10−7.55 (m, 10 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.3 (Me), 24.7 (CH_2), 26.5 (CH_2), 42.1 (CH_2), 42.5, 47.6 (CH_2), 48.2, 57.7, 66.2, 67.7, 69.6, 70.0, 71.1 ($PhCH_2$), 71.4 ($PhCH_2$), 72.3, 73.2, 102.8 (CO_3), 127.2, 127.7, 128.3, 137.2, 137.6, 213.2 (C=O) ppm. The camphorsulfonate **27** (0.146 g, 0.25 mmol) was heated with sodium methoxide (0.150 g, 2.78 mmol) in methanol (3 mL) under reflux for 24 h. Usual workup, followed by chromatographic purification with 20% ethyl acetate/light petroleum as eluent, yielded the known[11b] dibenzyl ether L-29 as a gum (0.083 g, 90%). $[\alpha]_D^{25}$ = −8.0 (*c*= 1, EtOH); ref.[11b] $[\alpha]_D^{25}$ = −8.4 (*c*= 1, EtOH). The orthoformate derivative **L-29** (0.083 g, 0.22 mmol) was stirred with trifluoroacetic acid/water (4:1 v/v, 0.5 mL) at room temperature for 24 h. The dibenzyl ether L-30[11b] was obtained (0.080 g, 99%) after evaporation of the solvents under reduced pressure; m.p. 144−145 °C. $[\alpha]_D^{25}$ = −27.3 (*c*= 1, EtOH); ref.[11b] m.p. 145−146 °C. $[\alpha]_D^{25}$ = −29.3 (*c*= 1.3, EtOH).

D-2,4-Di-*O*-benzyl-*myo*-inositol (D-30): The camphorsulfonate **26** (0.200 g, 0.33 mmol) was reacted with benzyl bromide (0.4 mL, 3.36 mmol) and silver(I) oxide (0.760 g, 3.28 mmol) in DMF (1 mL). The product obtained was chromatographed over silica gel (eluent: 5% ethyl acetate/light petroleum) to yield the dibenzyl ether **28** as a gum (0.145 g, 76%). $[\alpha]_D^{25}$ = +33.5 (*c* = 1, $CHCl_3$). ^1H NMR (200 MHz, $CDCl_3$): δ = 0.76 (s, 3 H, Me), 1.00 (s, 3 H, Me), 1.20−1.35 (m, 1 H), 1.45−1.65 (m, 1 H), 1.80−2.15, (m, 3 H), 2.20−2.45 (m, 2 H), 2.90 (d, *J* = 15.1 Hz, 1 H, SO_2CH_2), 3.55 (d, *J* = 15.2 Hz, 1 H, SO_2CH_2), 4.00 (dd, *J* = 3.2 Hz, 1.5 Hz, 1 H), 4.20−4.35 (m, 2 H), 4.40−4.85 (m, 4 H, $PhCH_2$ and 2 Ins H), 4.60−4.80 (q, *J* = 20.3 Hz, 12.1 Hz, 2 H), 5.40 (m, 1 H, H-4), 5.55 (d, *J* = 1.3 Hz, 1 H, HCO_3), 7.10−7.55 (m, 10 H, Ph) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.2 (Me), 24.5 (CH_2), 26.4 (CH_2), 42.0 (CH_2), 42.3, 47.5 (CH_2), 47.8, 57.5, 65.8, 67.3, 69.5, 69.9, 71.1 ($PhCH_2$), 72.1, 72.9, 102.6 (CO_3), 127.0, 127.8, 128.1, 137.0, 137.2, 213.5 (C=O) ppm. The camphorsulfonate **28** (0.140 g, 0.24 mmol) was heated with sodium methoxide (0.150 g, 2.78 mmol) in methanol (3 mL) under reflux for 24 h. The usual workup, followed by chromatographic purification with 20% ethyl acetate/light petroleum, yielded the dibenzyl ether **D-29** as a gum (0.084 g, 95%).

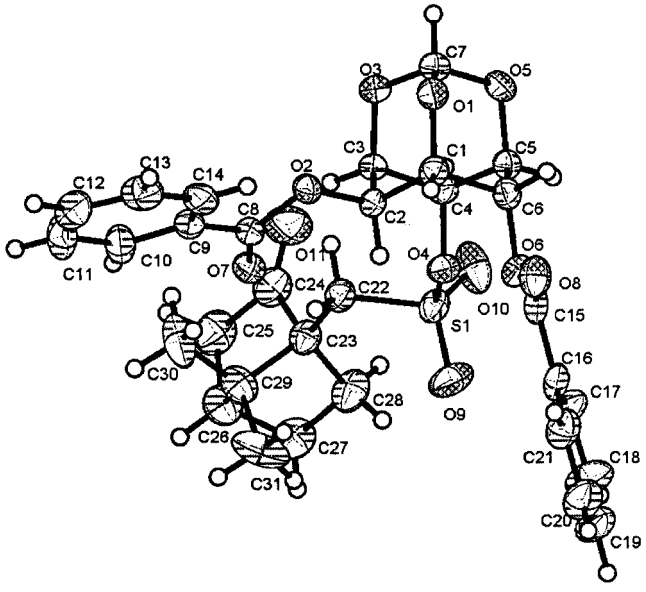


Figure 1. ORTEP plot of **26** with 30 % probability of thermal ellipsoids

$[\alpha]_D^{25}$ = +8.8 (*c* = 1.1, EtOH). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.60−3.70 (d, *J* = 9.9 Hz, 1 H, OH), 3.90 (m, 1 H), 4.20−4.35 (m, 2 H), 4.35−4.45 (m, 3 H), 4.45−4.60 (q, *J* = 10.9 Hz, 2 H, CH_2), 4.60−4.85 (q, *J* = 12.1 Hz, 2 H, CH_2), 5.53 (d, *J* = 1.4 Hz, 1 H, HCO_3), 7.20−7.50 (m, 10 H, Ph) ppm. The orthoformate derivative **D-29** (0.080 g, 0.22 mmol) was stirred with trifluoroacetic acid/water (4:1 v/v, 0.5 mL) at room temperature for 24 h. The known[11b] dibenzyl ether **D-30** was obtained (0.077 g, 99%) after evaporation of the solvents under reduced pressure; m.p. 145−146 °C. $[\alpha]_D^{25}$ = +29.3 (*c* = 1.3, EtOH); ref.[11b] m.p. 145−146 °C. $[\alpha]_D^{25}$ = +29.5 (*c* = 1.3, EtOH)].

X-ray Crystallography: Single-crystal X-ray data for **26** (Figure 1 and Table 1) were collected on Bruker SMART APEX Area Detector with graphite monochromated (Mo-K_α= 0.71073 Å) radiation. Cell refinement, data reduction, and structure solutions were carried out with the SAINT program. The empirical absorption corrections were applied using the program SADABS. The structure solution and least-squares refinement were performed using SHELXTL.[13] Hydrogen atoms were fixed stereochemically and refined using the riding model option. CCDC-188278 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data and data collection parameters for **26**

Empirical formula	$C_{31}H_{32}O_{11}S$
Molecular mass	612.63
Color, habit	Colorless, thin plates
Crystal size/mm	0.33 × 0.30 × 0.04
Crystal system	Monoclinic
a/Å	11.290(3)
b/Å	19.687(5)
c/Å	13.314(4)
α/degree	90
β/degree	97.123(4)
γ/degree	90
V/Å^3	2936.4(14)
Space group	$P2_1$
Z	4
F(*000*)	1288
$d_{calcd.}$ mg/m^3	1.386
μ/mm^{-1}	0.172
Data Acquisition	
Temperature/K	293(2)
Unit-cell reflections	6008
θ range/degree	2.333 to 24.334 deg.
Max. θ (deg) for reflections	25.000 deg
hkl range of reflections	$-13 \le h \le 12$, $-17 \le k \le 23$, $-15 \le l \le 15$
Reflections measured	14096
Unique reflections	8407
Reflections with $I > 2\sigma(I)$	7136
Absorption correction	Multi scan
Max. and min. transmission	0.9931 and 0.9446
Refinement on solution method	Full-matrix least-squares on F^2
H-atom treatment	Riding model
No. variables in L.S.	779
k in $w = 1/(\sigma^2F_o^2 + k)$ [$P = (F_o^2 + 2F_o^2)/3$]	*k* in $w = 1/[\sigma^2F_o^2 + (0.0515 \times P)^2 + 0.00 \times P$
R, R_w, gof	0.0512, 0.1228, 1.006
Density range in final Δ-map/e Å^3	0.375 and −0.345 e·A^{-3}
Final shift, error ratio	0.000
Sec. extinction type	Not applied

Acknowledgments

TD and KMS are recipients of fellowships from the University Grants Commission and the Council of Scientific and Industrial Research, New Delhi, respectively. M. S. S. thanks the Director, National Chemical Laboratory, for a grant. We thank Mr. Abhay Ghanekar for technical assistance.

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Received June 27, 2002
[O02355]